SEPARATION OF PHENOLIC COMPOUNDS FROM COAL LIQUIDS

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INTRODUCTION

Coal liquids contain considerable amounts of phenolic compounds which are industrially important chemicals. Upgrading of coal liquids have been performed by catalytic hydrogenation to produce fuel oils of good quality. Because of the existence of phenolic compounds, the upgrading requires hydrogen in quantity. Thus, an economical and effective method for separation of these compounds from coal liquids has been expected to develop. Here we report that a solvent extraction of phenolic compounds from naphtha distillates of coal liquids using methanol and water as solvents (1). The present presentation discusses the experimental conditions for the effective separation and the composition of the products.

EXPERIMENTAL

Materials. Feed oils, naphtha distillates of Battle River and Wandoan coal liquids, were supplied by a 1 t/d plant of Sumitomo Metal Ind. Ltd. The boiling range of each sample is IBP-185 °C. The distribution of acidic compounds in the feed oils is summarized in Table 1. Methanol (99.6 % pure) and dichloromethane (99.0 % pure) were from Wako Pure Chemical Ind. Ltd. and used without purification.

Procedure for solvent extraction. Scheme 1 shows the procedure of the present separation. To a mixture of a feed oil (5.0 mL) and methanol (5-20 mL) was added water (5-40 mL) at 30 °C. The resulting mixture immediately separated into two layers of a methanol-water layer and an oil layer. Phenolic compounds in a feed oil were extracted into the methanol-water layer. After 10 min, the methanol-water layer was taken out and evaporated to remove methanol. The aqueous phase was extracted with dichloromethane (30 mL x 3). The extracts were dried over sodium sulfate. Filtration and removal of the solvent gave a mixture of phenolic compounds as a brown oil. The compound distribution and selectivities of phenolic compounds in the products were determined with a gas chromatograph using a Shimadzu 50-m HR-101 (corresponding to OV-101) capilary column and a Shimadzu FAP-S 3.1-m x 3 mm packed column.

RESULTS AND DISCUSSION

Effect of solvents on the percent extraction

Methanol. When the feed oil was treated with water, only 20 % of phenolic compounds were extracted. However, extraction of a mixture of the feed oil (5 mL of a Battle River naphtha) and methanol (5-20 mL) with water (5 mL) gave better results in the extraction percents as shown in Fig. 1. The percent extraction was determined by the comparison of phenolic compounds separated

as a mixture with those contained in the feed oil. The yields increased significantly with the amount of methanol. There must be an appreciable interaction between phenolic compounds and methanol in the mixture of the feed oil and methanol. Addition of water caused phase separation to give an oil layer and a methanol-water layer rich in phenolic compounds. The methanol-water layer contained larger amounts of phenolic compounds with the increase of methanol. Removal of methanol and subsequent extraction with dichloromethane of the resulting aqueous solution gave a mixture of phenolic compounds as a brown oily product. It is noteworthy that the extraction of phenolic compounds from an aqueous solution with dichloromethane gave these compounds in 90 % or above under the present conditions.

Water. Fig. 2 shows the results of the extraction using the feed oil (5 mL), methanol (5 mL), and water in the range of 5 to 40 mL. The percent extraction of phenolic compounds increased with the amount of water. However, the yield was reached to the limmiting value of about 40 %. Thus, methanol gave a stronger effect than water on the yields of the phenolic compounds.

Effect of solvents on the compound distribution

The effects of the amounts of the solvents on the distribution of the phenolic compounds in the separated products was examined. The results of the distribution of the representative compounds, phenol and o-cresol were shown in Fig. 3 and 4. These results indicate that the changes of the amounts of methanol and water gave little influence on the distribution. These values of the distribution (about 36 % for phenol and about 10 % for o-cresol) correspond with those of the distribution of acidic components in the feed oil. Similarly, other compounds, m, p-cresol, o, m, and p-ethylphenol were extracted efficiently, corresponding with the distribution of the acidic components as shown in Table 2.

Application

The present method can be applied to the separation of nitrogen compounds in middle distillates of coal liquids (2) and in coal tar (3). Nitrogen compounds such as quinoline and indole can be extracted efficiently.

In summary, the solvent extraction using methanol and water is easy to perform. All solvents can be recovered. The present method provides a new effective method for the industrial separation of phenolic compounds from coal liquids.

References

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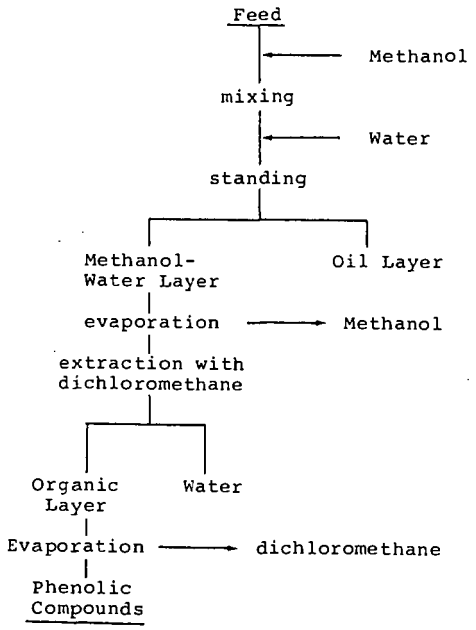
2) Y. Kodera, K. Ukegawa, and T. Takahashi, 1989 International Conference on Coal Science, Tokyo, Oct. 24, 1989.
3) K. Ukegawa, A. Matsura, K. Yazu, and T. Kondo, 1989 International Conference on Coal Science, Tokyo, Oct. 24, 1989.

Table 1 Characteristics of naphtha distillates

	Battle River	Wandoan
Acidic components, wt%	22.5	13.8
Compounds distributuion of acidic components, wt% a)		
phenol	39.4	36.6
o-cresol	12.5	13.3
m-cresol	19.8	14.2
p-cresol	17.3	15.6
o-ethylphenol	1.2	1.5
m-ethylphenol	3.5	6.0
p-ethylphenol	1.7	3.7
others	4.6	4.1

a) The distribution was determined by GC.

Scheme 1 Procedure for the solvent extraction



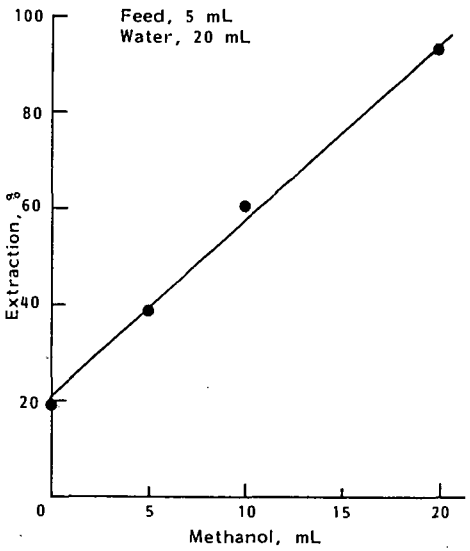


Figure 1 Effect of methanol on the percent extraction

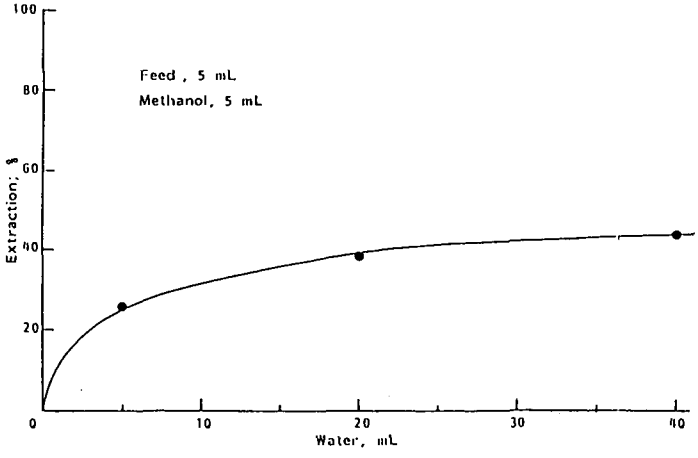


Figure 2 Effect of water on the percent extraction

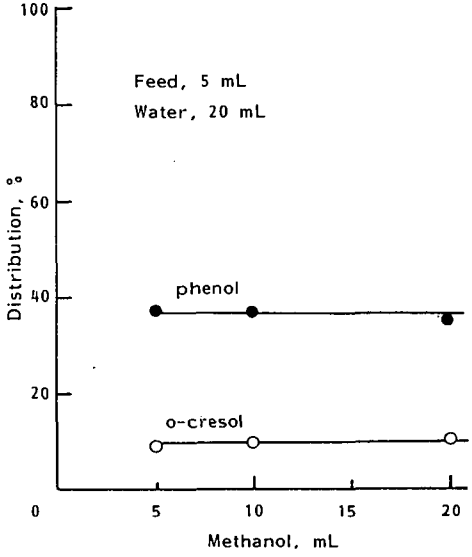


Figure 3 Effect of methanol on the compound distribution

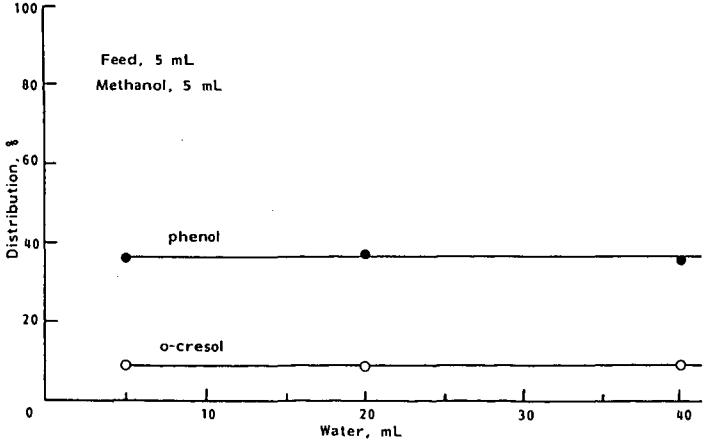


Figure 4 Effect of water on the compound distribution

Table 2 Compound distribution in the separated products

Entry	Methanol mL	Water mL	Distribution, % cresol(m,p)/ethylphenol(o,m,p)
1	5	5	16.9, 12.1 / - , 2.9, 1.7
2	5	20	15.9, 11.4 / - , 2.2, 1.2
3	5	40	16.8, 11.8 / 1.0, 2.3, 1.5
4	10	20	17.5, 12.7 / 1.4, 2.9, 1.4
5	20	20	18.3, 12.7 / 1.5, 3.2, 1.2